

An Initial Set of Working Hypotheses Concerning Some Chemical, Physical and Thermodynamic Phenomena That Occur When CO₂ Is Injected Into A Coalbed

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There is a fundamental lack of understanding concerning the physical, chemical and thermodynamic phenomena that occur when CO₂ is injected into a coal seam. This lack of understanding prevents us from developing the best possible models of the process; it prevents us from making sense of operational problems that occur during production and it prevents us from taking the best possible actions to surmount operational problems. In fact, the "Carbon Sequestration Technology Roadmap Pathways to Sustainable Use of Fossil Energy" identifies CO₂ flow and storage in coals as "not well defined" and describes the effects of CO₂ on coal reservoir permeability as uncertain.¹ These are barrier issues with respect to wide scale development and implementation of sequestration of CO₂ in coal seams. When Burlington Resources performed a commercial scale CO₂-ECBM/sequestration project in the Allison Unit in northern New Mexico they encountered unforeseen operational problems. An initial CO₂ injection rate of about 5 MMcf/d was used but was reduced to 3 MMcf/d due to loss of injectivity. "Subsequent to that, injectivity began a long period of improvement, which has continued through the last available data. These trends are consistent for all four injection wells."² CO₂ was injected for 6 months during which an abrupt increase in water production was immediately noticed. After 6 months, injection of CO₂ was stopped. During the first 6 months of operations "5 of the production wells were temporarily shut in to facilitate CO₂/CH₄ exchange in the reservoir."³ As a consequence of the above, we formulated a number of hypotheses that describe the chemical, physical and thermodynamic phenomena that occur when CO₂ is injected into a coal seam. These hypotheses can be used to develop models that more accurately simulate the CO₂-ECBM/sequestration process. A more complete understanding of what occurs when CO₂ is injected into a coal seam is needed to understand the causes of operational problems when they occur, and to take the most appropriate steps to resolve them. White has described these hypotheses in preliminary form in a recent publication,⁴ and in more detailed form.⁵

Hypotheses

- 1) The glass-to-rubber transition temperature (T_g) of the coal will be dramatically reduced by imbibition of CO₂. The coal will become plasticized.⁶
- 2) The cleat system within the coalbed will begin to close and become restricted, slowing Darcy flow within that area of the seam due to swelling.
- 3) There will be a substantial increase in the self diffusivity of CO₂ in coal once it has become plasticized and is above its T_g .^{6,7}
- 4) The diffusivity of CO₂ in coal swollen by high pressure CO₂ can be described by free volume theory.
- 5) The degree to which plasticization, swelling, increased diffusivity, lowering of T_g , relaxation of the macromolecular network, and depression of the softening temperature occur will be limited by the degree that the coal is free to swell.
- 6) Both liquid and supercritical CO₂ moving through a coalbed will extract small molecules trapped within the macromolecular network. As the network relaxes, these molecules will be released and move with the flowing CO₂ as long as the pressure is above their threshold pressure.
- 7) Some of the minerals commonly found in coal will dissolve in the acidic, carbonated formation water during those times when both water and high pressure CO₂ are present together in the coal.
- 8) The Ca and Mg content of the coal will decrease due to dissolution of carbonate minerals by carbonic acid and due to Ca and Mg being displaced from carboxylic acids in low rank coal.

- 9) Injection of dry CO₂ will dry the coal, particularly in those areas where the flow rate of CO₂ is highest.
- 10) There will be a CO₂ pressure, temperature and pH gradient across the coalbed from the injection well to the recovery well. The temperature gradient is due to Joule-Thompson cooling. When dissolved minerals and organics reach areas of the seam with lower pressure they will precipitate, clogging the coal's pores.

Possible Effects of CO₂ Adsorption on the Glass-to-Rubber Transition Temperature and Softening Temperature

Coals exist as either a glass or as a flexible rubber depending on the temperature and other factors. The glassy state is characterized by brittleness, little or no large segmental molecular motion throughout the macromolecular network. Diffusion throughout the system is slow and diffusivity of guest molecules is highly dependent upon their molecular size and thus their molecular weight. Individual components of the macromolecular network are held together by non-covalent interactions such as van der Waals forces that are of sufficient strength to prevent movement with the exception of local vibrations and rotations.^{6,7} Conversely, when in the rubbery state, sufficient thermal energy is available to surmount the non-covalent interactions. Then the macromolecular system is free to move, allowing the coals to become flexible, internal molecular motion becomes liquid like, diffusion is much more rapid and the dependence of guest molecule diffusivities on molecular size is much reduced.^{6,7}

The temperature at which a coal is transformed from a glass to a rubber is known as the glass-to rubber-transition temperature (T_g). When coals and other macromolecular systems such as polymers imbibe small molecules like CO₂ their T_g can be decreased (hypothesis 1). The physical and chemical properties of coal change depending upon the state it is in, glass or rubber. The molecular transport dynamics of guest molecules are greatly effected. CO₂ induced depression of the glass transition temperature and other plasticization effects have been investigated in a variety of systems.^{8,9} When coal imbibes CO₂, it swells (hypothesis 2). The CO₂ acts as a plasticizer depressing T_g causing a structural rearrangement of the macromolecular system. Plasticizers add free volume and molecular mobility, converting a glass into a rubber. Once coal is plasticized by CO₂, it rearranges and moves to a lower energy where it displays different adsorption properties toward CO₂. Upon imbibing CO₂ and swelling, the softening temperature of the coal is depressed, as shown graphically in Figure 1.¹⁰ CO₂ lowers the T_g by acting as a plasticizer, dissolves in the coal, the structure rearranges and relaxes and the softening temperature decreases. As shown in Figure 1, at low CO₂ pressures there is little or no effect on softening temperature. However, at higher pressures, around 3 MPa, the effect is dramatic. The softening temperature is decreased over 300 K from something greater than 673 K to less than 373 K.

Hsieh and Duda¹¹ showed that fluids are imbibed by coal in three stages. There is a rapid surface adsorption, presumably at least in part into the pores, followed by a slow diffusion of fluid into the coal, followed by relaxation of the macromolecular network and additional diffusion of the fluid.¹¹ Reucroft and Sethuraman¹² showed that CO₂ dissolves in coal and is not simply adsorbed on the surface. Table 1 shows that swelling increases as the carbon content of the coal decreases and as rank decreases. Reucroft and Sethuraman also showed that swelling continues to increase with time for about 200 hours as more CO₂ is imbibed into the macromolecular structure, as pressure increases swelling increases and as pressure increases the time required to reach equilibrium swelling decreases.¹²

Effect of CO₂ Adsorption on Organic Matter

When CO₂ interacts with coal, multiple processes occur. CH₄ desorption occurs simultaneously with CO₂ adsorption. CH₄ is displaced into the cleat system of the coal where it begins to move toward an area of lower pressure, the production well. CH₄ desorption causes coal to shrink, whereas CO₂ adsorption causes the coal to swell and the macromolecular structure to relax.⁶ In general, coal swelling due to CO₂ sorption is greater than shrinkage caused by CH₄ desorption (hypothesis 2). The net effect is coal swelling. Weak intermolecular interactions such as van der Waals interactions, hydrogen bonds and charge transfer interactions between one part of the macromolecule and another or between two macromolecules are broken and replaced by interactions between the macromolecule and CO₂. This allows the small molecules trapped

within the interwoven macromolecular network to be released, so that they are free to move. Liquid and dense gaseous CO₂ are excellent solvents. As the trapped molecules are released, they become solvated and extracted by the CO₂, and migrate with CO₂ throughout the coalbed (hypothesis 6). The extraction process and movement of formerly trapped molecules begins with the lower molecular weight compounds first. Movement of compounds is a function of each compound's threshold pressure. The threshold pressure of a substance was originally defined by Giddings as the lowest supercritical pressure that will cause a substance to just begin migrating in a flowing stream of supercritical fluid.¹³ Among hydrocarbons, the threshold pressure is an approximate function of their molecular weight. Generally, the amount extracted from coal is quite small, about 2.5 weight percent or less.

Effect on Diffusivity

The plasticization effects of CO₂ on coal (hypotheses 1 and 3) are discussed elsewhere.⁶ Hypothesis 3 is an extension of one proposed by Larsen to include the self diffusion of CO₂ in plasticized coal. Mass transport through coal is a controlling function during the sequestration of CO₂. If the cleat fracture system becomes restricted due to swelling, then Darcy flow will be restricted and transport through the coal will be primarily Fickian (hypothesis 2).

A substantial increase in molecular diffusivity of guest molecules in macromolecular systems in contact with supercritical CO₂ has been documented recently. The diffusivity of ethylbenzene in CO₂ swollen polystyrene shows a 10⁶ fold increase when supercritical CO₂ is present.¹⁴ Experimental information that defines factors that impact and control transport properties in CO₂ swollen macromolecular systems is limited for polymeric systems and to our knowledge, unknown for coals. Transport properties of Co(II) complexes in polymeric systems in contact with supercritical CO₂ are dependent upon the degree of CO₂ swelling and the degree of plasticization.⁹ These are plasticization induced changes in the transport properties of guest molecules in the swollen macromolecular network. We hypothesize that the substantial increases in diffusivity of guest molecules in polymeric systems applies to the self diffusion of CO₂ in CO₂ swollen macromolecular systems such as coal. As such, we expect diffusion of CO₂ in coal swollen by high pressure supercritical CO₂ will be much more rapid than in the same coal before plasticization (hypothesis 3).

The CO₂ swollen polymeric systems described above were unconfined and free to swell. Similarly, the coal in the softening point depression experiment performed by Khan and Jenkins was free to swell.¹⁰ A coal seam is a relatively fixed volume system, in which coal is confined and not free to swell. Therefore, plasticization, swelling, increased diffusivity, lowering of T_g, relaxation of the macromolecular network, and depression of the softening temperature will be confined and limited to the degree that the coal is free to swell. The only volume available to swell into is the cleat volume in the seam. Cleat volume is generally 0.2 to 2.0 volume %.¹⁵⁻¹⁹ The pore volume is also available, but usually amounts to less than 10% of the coal volume. Thus, we expect that the confined space will limit the degree the coal can swell, and will thus limit the increase in CO₂ diffusivity and possibly limit the other plasticization induced changes a coal may undergo (hypothesis 5).

Lee *et al.*⁹ showed that in a polymeric system swollen by CO₂, the effect of CO₂ swelling on mass transport can be understood using free volume theory. They estimated the fractional free volume (FFV) of swollen polymeric system from the following relationship:

$$FFV = \frac{V_m - V_w}{V_m} \quad [1]$$

where $V_m = M/d$ is the molar volume of the swollen polymer, M and d are the molecular weight and density of the swollen polymer, and V_w is the estimated van der Waals volume. CO₂ diffusivity should decrease exponentially with the reciprocal free volume, $1/FFV$. As swelling increases, free volume increases and diffusivity increases. The same theoretical approach may explain CO₂ diffusion in supercritical CO₂ swollen coals, and allow estimation of the CO₂ diffusivity under a variety of conditions in swollen coal matrices (hypothesis 4).

Effect of CO₂ Adsorption on Mineral Matter

High pressure CO₂ and water can have a profound effect on the mineral matter present in coal. Many minerals present in coal are soluble in acidic aqueous solutions (hypothesis 7). The solubility of CO₂ in water and brine is substantial at high pressures, see Figure 2. According to simulations performed, the pH of CO₂ solutions in pure water and brine at 10.1 MPa and 318 K is approximately 3.1 in pure water and about 2.9 in brine, see Figure 3. Alkaline earth metals are removed from coal by treatment with acidic aqueous solutions. Calcite, dolomite, and other carbonate minerals are removed from coal at room temperature by extraction under acidic conditions with aqueous CO₂ solutions. The solubilities of some minerals common to coal in carbonated water and brine solutions at various pressures of CO₂ at 323 K are shown in Figure 4. The solubility of carbonate minerals in carbonated brine was estimated using Geochemist's Workbench (GWB)²⁰ while the solubility of other coal associated minerals and clays was estimate using PHREEQC (pH-REdox EQUilibrium equation program in C language).²¹

Hayashi *et al.*²² studied the removal of Ca and Mg from several low rank coals by batch extraction with CO₂ dissolved in water at 600 kPa and 298 K at various extraction times, see Figure 5. They showed that the Ca removal yield is affected by the total Ca content of the coal and the total carboxyl content. Ca removal is also affected by the coal:water ratio in that Ca removal decreases as the amount of water decreases. During CO₂ sequestration in coal, it is expected that the water content of the coal will initially decrease with time. The coal will most probably be dewatered before CO₂ injection. This process will remove some of the bulk water in the cleat system. After CO₂ injection begins, we expect that the remaining water in the cleat system and the water present in the pores will be reduced. This is consistent with the field results observed during the Burlington Resources commercial CO₂-ECBM/sequestration project. When CO₂ injection began, water production increased. The rate and extent of these processes are unknown. The Ca and Mg content of the coal will be reduced when both water and CO₂ are present (hypothesis 8). The dissolved minerals will be transported through the coal seam and eventually recovered in the produced water when the process is taken to completion. As the water content decreases, the amount of Ca and Mg removed will decrease. If water migrates back into the seam, then Ca and Mg removal could increase. The solubility of carbonate minerals in acidic aqueous solutions requires both H₂O and CO₂.

Drying of Coal by Flowing CO₂

Iwai *et al.* report the use of supercritical CO₂ to dry coal.²³ Water is removed by either dissolving in the CO₂ or by being displaced by it. Water is only sparingly soluble in supercritical CO₂. Under some conditions water is almost quantitatively removed from low rank coals. Iwai *et al.* showed that drying of ground and sieved coal (8 grams, 1000 μ m - 595 μ m) with CO₂ (1.5 moles/hour for 20 hours) at either 9.8 or 14.7 MPa and 313 K removed water and increased the surface area and the pore volume of the coal, as shown in Table 2. The degree of coal drying that will occur during CO₂-ECBM/sequestration is unknown, but will probably not be quantitative except near the injection well (hypothesis 9). Water removed during the dewatering process and that removed by CO₂ can be eventually replaced by recharge of water from aquifers. In areas of the seam that are at pressures higher than the surrounding hydrostatic pressure, re-invasion of water is expected to be slow.

Precipitation Due to the Pressure Drop

There will be both a pressure drop and a CO₂ partial pressure drop from the point of injection to the production well (hypothesis 10). The injected CO₂ follows the path of least resistance, moving from areas of high pressure near the injection well to those of lower pressure (toward the production well) through the areas of the coalbed that have the highest permeability. As injection continues, the areas of highest permeability initially become less permeable with time because the swelling process begins to close the cleat system which initially controls gas transport within the coalbed. Extracted compounds that are moving with the flowing CO₂ will begin to clog or plug the coal's pores (hypothesis 10).²⁴ The effect of this pore clogging on permeability is unknown. The back pressure increases due to closing of the cleat system caused by initial swelling. CO₂ begins to flow into other areas of the coalbed that now represent

areas of higher permeability. Eventually, many areas of the cleat system become restricted. When this happens, the pressure across the coalbed rises, increasing the density and solvating power of the CO₂, which is directly related to its pressure and density. The precipitated components then begin to redissolve according to their threshold pressure. As the redissolution process occurs, flow begins again from areas of high pressure toward the production well. CO₂ moves through the coal as a front, probably with fingering, similar to frontal chromatography. The partial pressure of CO₂ will be high in areas behind the front and at the front, but low ahead of the moving CO₂ front. When dissolved carbonate minerals migrate to areas of lower CO₂ partial pressure and/or decreased amounts of water they will precipitate out of solution and initiate the clogging process.

Eventually, the flowing CO₂ finds its way to the area of lowest pressure at the production well, causing the CO₂ density and solvent strength to decrease. This causes the dissolved organic molecules and minerals to precipitate again when the pressure becomes less than their threshold pressure, clogging the coal matrix adjacent to the production well. Eventually, these molecules will be re-extracted as the CO₂ pressure builds up behind them, redissolving them and moving them into the production well. The Ca and Mg content of the produced water may not increase until the CO₂ front has migrated into close proximity of the production well. Ca and Mg containing minerals will precipitate out of solution rapidly as the pH increases due to loss of CO₂ pressure at the production well, eventually forming carbonate scale in the production well if production is taken to finality.

It is important to note that these are only initial hypotheses that await additional experimental confirmation from the lab and field.

Tables

Table 1. The behavior of a bituminous coal, a subbituminous coal and a lignite in CO₂ at 298 K and CO₂ pressures of 0.5, 1.0, and 1.5 atm.¹²

Coal % Carbon	CO ₂ Pressure MPa	Coal Swelling Vol. %	% CO ₂ Dissolved in Coal
83.8	0.5	0.75	13.8
	1.0	0.85	16
	1.5	1.33	24
78.3	0.5	1.24	23
	1.0	2.23	41
	1.5	3.11	58
65.8	0.5	2.16	24
	1.0	3.00	32
	1.5	4.18	47

Table 2.: Drying of ground coal using supercritical CO₂ and thermal drying at 383 K.²³

Sample	Berau coal (g-water/g- dried coal)	Taiheiyo coal (g-water/g- dried coal)
Supercritical drying (14.7 Mpa)	0.0188	0.0100
Thermal drying (383 K)	0.0153	0.0091
Raw coal	0.2271	0.0622

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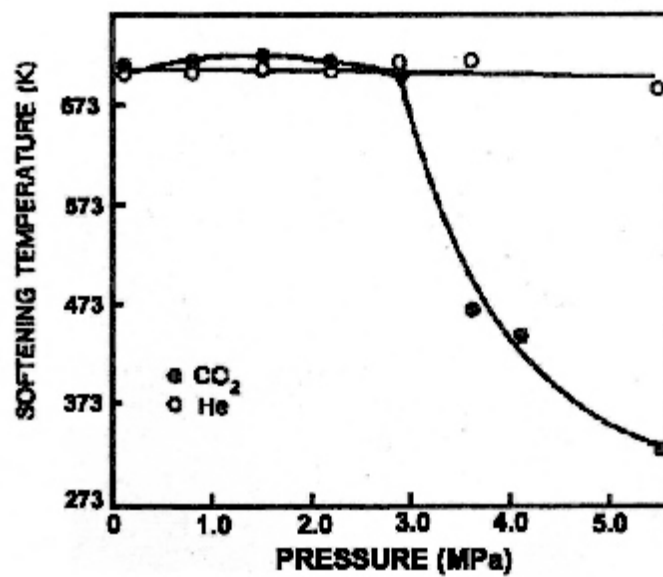


Figure 1. Depression of the softening point temperature of a coal in the presence of increasing pressures of both CO₂ ● and He ○.¹⁰

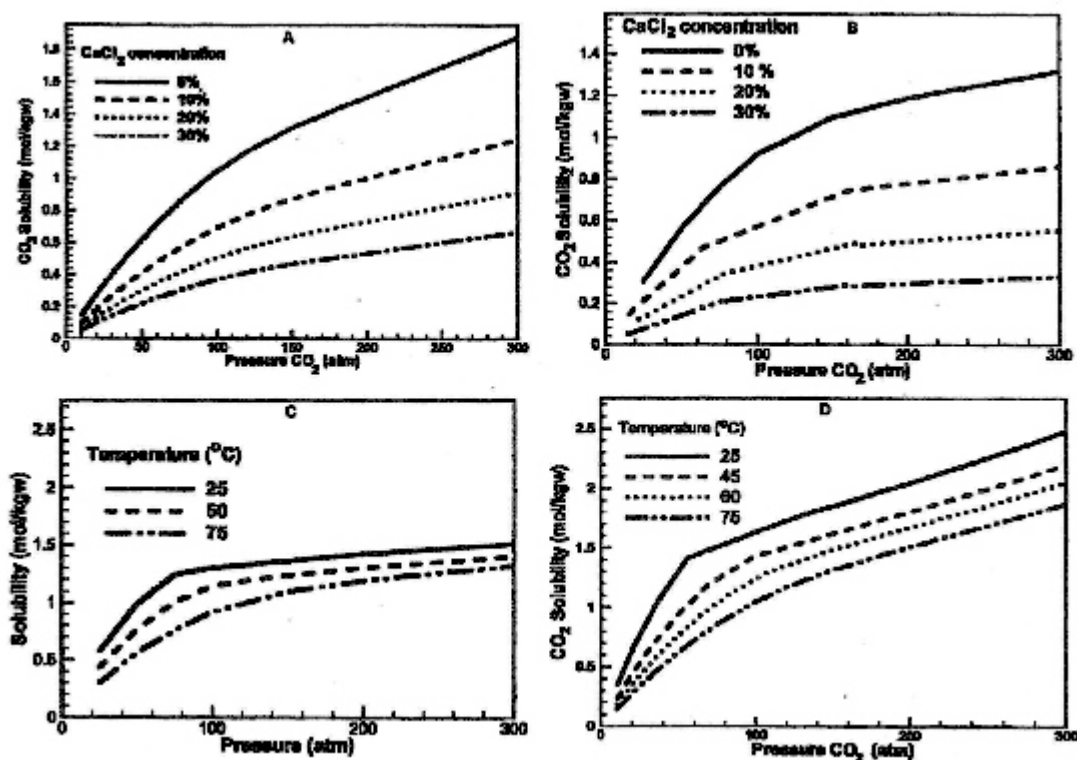


Figure 2. Solubility of CO₂ in pure water and brine as a function of pressure (A) at various concentrations (wt%) of CaCl₂ and 75°C- experimental results from Prutton and Savage.²⁵ (B) at various concentrations (wt%) of CaCl₂ and 75°C- calculated using the Geochemist's Workbench.© (C) in pure water at various temperatures- experimental results from Wiebe and Gaddy.^{26,27} (D) in pure water at various temperatures- calculated using PHREEQC.

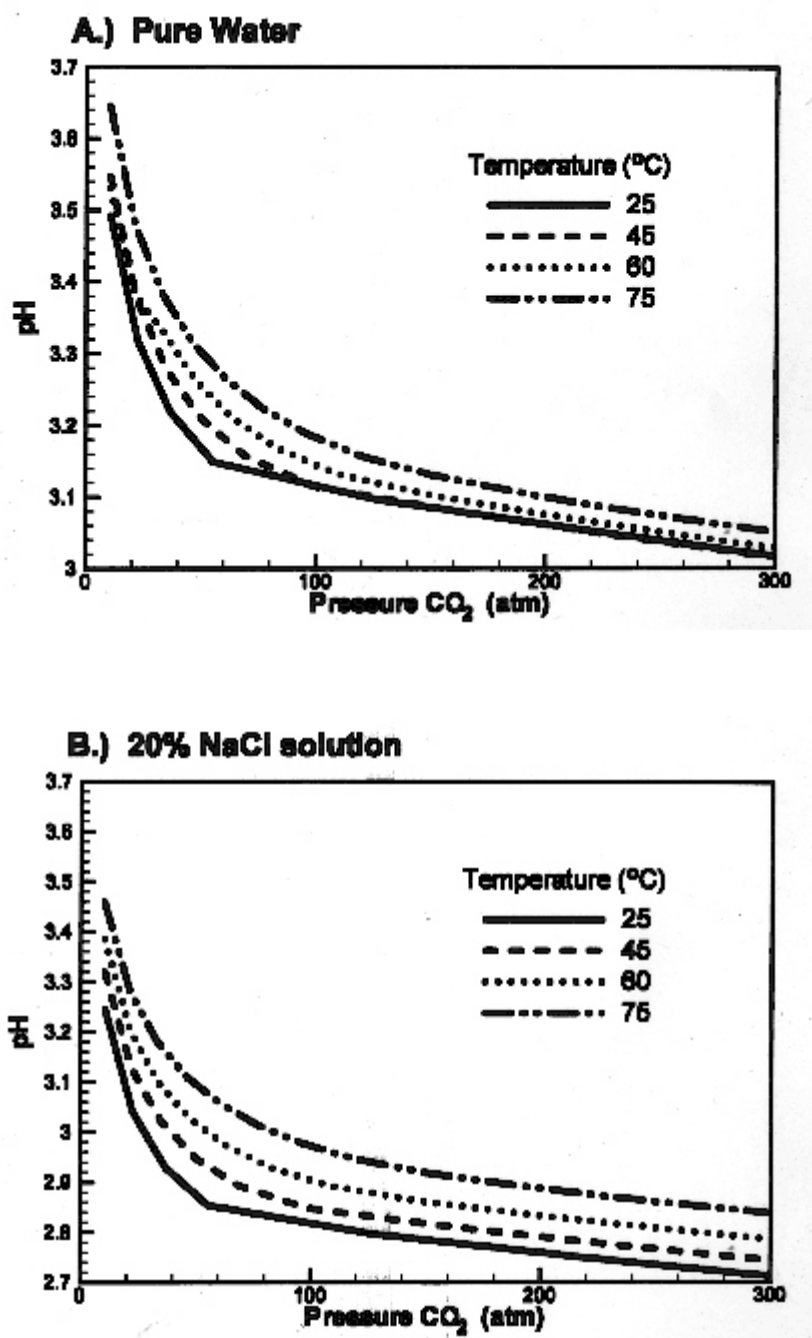
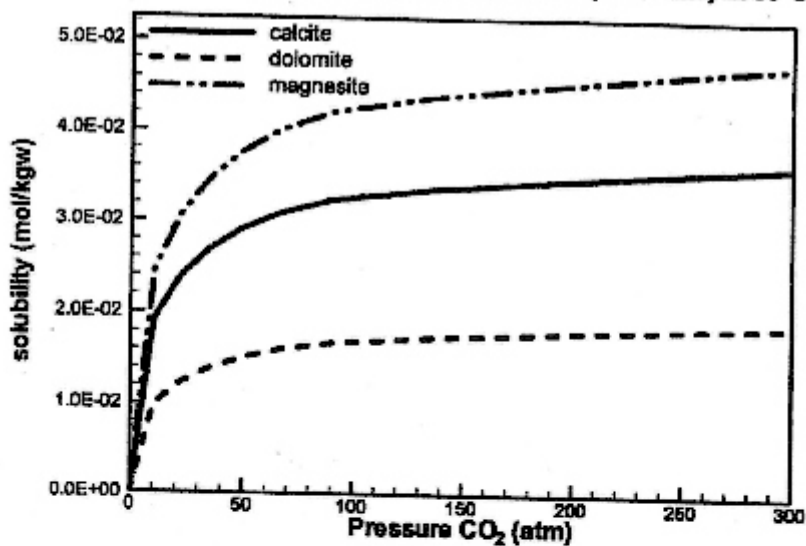


Figure 3. pH of carbonated water (A) and carbonated brine (water containing 20% NaCl) (B) as a function of pressure at 298, 318, 333, and 348 K. The results in pure water were estimated using PHREEQC while the brine results were estimated using Geochemist's Workbench.

A Solubility of Carbonates in Carbonated Brine (20% NaCl) at 50°C



B Solubility of Coal Associated Minerals in Carbonated Water at 50°C

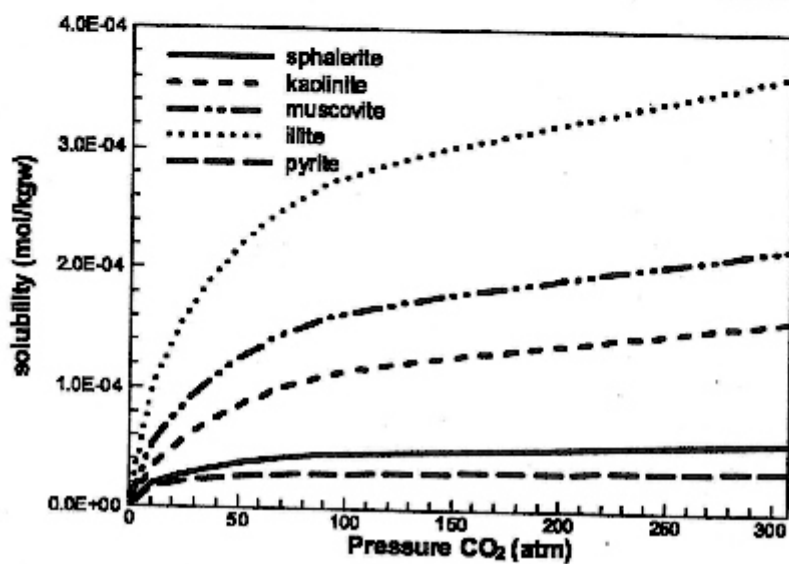


Figure 4. Solubility of calcite, dolomite and magnesite in carbonated water (A) and carbonated brine (water containing 20% NaCl) (B) as a function of pressure at 323 K. The results in pure water were estimated using PHREEQC while the brine results were estimated using Geochemist's Workbench.

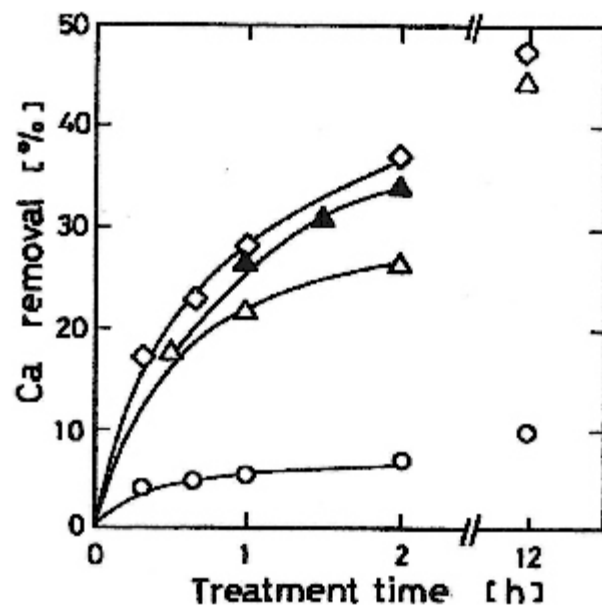


Figure 5. The removal of Ca from several coals by batch extraction with CO_2 dissolved in water at 0.6 MPa and 298 K at various extraction times.²² ○ Morwell coal; ◇ Taiheiyō coal; △ Wandoan coal.